

Chamberlain KA, Rankin KS, Briscoe A, Deehan D, Hyde PJ. [Wear properties of Poly-Ether-Ether-Ketone \(PEEK\) bearing combinations under zero and cross shear kinematics in total knee arthroplasty](#). *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 2018

Copyright:

This is the peer reviewed version of the following article: Chamberlain KA, Rankin KS, Briscoe A, Deehan D, Hyde PJ. [Wear properties of Poly-Ether-Ether-Ketone \(PEEK\) bearing combinations under zero and cross shear kinematics in total knee arthroplasty](#). *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 2018, which has been published in final form at <https://doi.org/10.1002/jbm.b.34136> This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

Date deposited:

18/05/2018

Embargo release date:

07 May 2019

1 **TITLE PAGE**

2 **Wear properties of Poly-Ether-Ether-Ketone (PEEK) bearing combinations under zero**
3 **and cross shear kinematics in total knee arthroplasty**

4 **AUTHORS**

5 Kathryn A Chamberlain^a, Kenneth S Rankin^b, Adam Briscoe^c, David Deehan^b, Philip J Hyde^a

6 **Corresponding Author:** Philip J Hyde Philip.hyde@newcastle.ac.uk

7 ^a Bioengineering Group, School of Engineering, Newcastle University, Stephenson Building,
8 Newcastle Upon Tyne, NE1 7RU, England, United Kingdom

9 ^b Freeman Hospital, Newcastle Upon Tyne, NE1 7DN, England, United Kingdom

10 ^c Invia Global Technology Centre, Hillhouse International, Thornton-Cleveleys, Lancashire,
11 FY5 4QD, England, United Kingdom

12 **ABSTRACT**

13 Poly-ether-ether-ketone (PEEK), having shown favourable biocompatibility in spinal
14 applications is being considered as an alternative biomaterial in orthopaedics, either as part of
15 an all-polymer bearing couple, or a replacement for the metallic component in hard-on-soft
16 bearings.

17 Throughout the literature ultra-high molecular weight polyethylene (UHMWPE) exhibits a
18 range of wear behaviour dependent upon the amount of cross shear (CS) present in the bearing
19 motion; in comparison, the behaviour of PEEK bearing combinations subject to cross shear
20 conditions is less understood.

21 The aim of this study was to investigate the effect of cross shear on PEEK-on-PEEK and
22 PEEK-on-Metal bearing couples. Wear tests were conducted using a four station pin-on-plate
23 rig capable of uni-directional motion (zero cross shear) and multi-directional motion (cross
24 shear); reciprocation (1 Hz), rotation (0 or 1 Hz), with gravimetric wear analysis used to
25 determine the wear factors.

26 The combined wear factors from the PEEK pins articulating on either PEEK or metal plates in
27 this study suggest that it is preferable to use PEEK-on-Metal bearing couples under zero cross
28 shear kinematic conditions and PEEK-on-PEEK for high cross shear applications. PEEK
29 appears to demonstrate a CS dependency when articulating on hard surfaces.

30 **Keywords:** PEEK, wear, all-polymer wear, cross shear, pin-on-plate

31 **Running Head:** Pin-on-plate wear tests of PEEK bearings subject to cross shear

INTRODUCTION

Highly polished metals such as cobalt chromium molybdenum (CoCrMo) and the polymer, ultra high molecular weight polyethylene (UHMWPE) make up the majority of artificial bearings in orthopaedics. Metal-on-Polyethylene (M-on-P) is currently the gold standard for total knee replacements (TKR) forming 82.3 % of all cemented TKRs in 2015-2016¹. However, wear of the UHMWPE component remains a concern².

UHMWPE wear debris is a major contributing factor in osteolysis (bone loss), leading to aseptic loosening, documented as the primary reason for failure in 40.2 % of knee replacements, reducing the longevity of the implant^{1,3}. Therefore, in order to increase the longevity of the implants there has been a drive to find alternative materials.

Research into a chemically inert polymer, poly-ether-ether-ketone (PEEK), is growing in popularity since its initial use in spinal applications revealed favourable biocompatibility^{4,5}. However, it should be noted that concerns about the use of PEEK-on-PEEK (PK-on-PK) self-mating devices in cervical total disc replacement (TDR) were reported by Kraft *et al*^{6,7} who found an increase in wear for PK-on-PK compared to UHMWPE-on-M with evidence of pitting and delamination. These observations were also noted by Grupp *et al*⁸ however, no increase in the wear between the PK-on-PK and UHMWPE-on-M was found. This was in agreement with Brown *et al*⁹ who found comparable results for PK-on-PK compared to the conventional UHMWPE-on-M. The behaviour of PEEK based bearings for other joints is less well known.

It is postulated that PEEK could offer a viable alternative bearing material for joint replacements as it has numerous advantages, such as: low weight, reduced complexity of the

manufacturing process (it can be moulded or extruded), and a reduced distortion in images from magnetic resonance and computed tomography scans compared to the current UHMWPE-on-M bearing couples¹⁰. Furthermore, the lack of any metal component in an all-polymer knee holds the potential to eliminate the risks of patients suffering from metal hypersensitivity.

With a Young's modulus (~4 GPa) closer to that of cortical bone (~18 GPa) than metal titanium alloy (110 GPa)¹¹ or CoCr (220 – 230 GPa)¹², the concept of an all-polymer TKR with PEEK replacing the metal femoral component has been explored with initial wear tests showing promising results¹³. Theoretically all-polymer knee replacements should reduce stress shielding on the host bone after TKR, offering an attractive alternative to current TKR designs in addition to reduced machining manufacturing costs^{14,15}. To fully determine the bio-tribological characteristics of PEEK, it is important to study the effects of cross shear (CS), defined as multi-directional sliding motion of the bearing surfaces, on the wear rate¹⁶. Zero CS refers to a purely linear, uni-directional sliding motion with the addition of coupled rotation resulting in multi-directional motion CS.

It is well known that UHMWPE exhibits a range of wear behaviour dependent upon the amount of CS present in the bearing motion, with wear factors for linear motion two to three orders of magnitude lower than those found from multi-directional motion tests, matching those found clinically, typically $\times 10^{-8} \text{ mm}^3/\text{Nm}$ and $\times 10^{-6} \text{ mm}^3/\text{Nm}$ respectively^{17,18}. This can, therefore, be misleading if used to predict *in-vivo* wear, but can also be exploited in the design of, for example, rotating platform knees, where the very low CS level in the separated bearings structure reduces wear. Theoretically, when subjected to zero CS the polymer chains at the surface of an UHMWPE bearing may become aligned in the principle direction of motion,

leading to strain hardening and a decrease in wear^{18,19}. In comparison to UHMWPE, the behaviour of PEEK bearing combinations under a range of CS conditions that are physiologically relevant is much less understood.

A study by Baykal *et al.*²⁰ investigated the effect of CS on PEEK on highly cross-linked polyethylene (PK-on-HXLPE) and HXLPE-on-PK using a pin-on-disc test rig, with alpha calf serum as the lubricant, and found that the wear rate of PK-on-HXLPE was not affected by the introduction of CS. A more recent PK-on-CoCr pin-on-plate (PoP) study by Brockett *et al.*²¹ found PEEK appeared to have a cross shear dependency with the wear of PEEK increasing with an increase in CS ratio, however, this was not reported as statistically significant. In the present study, a clear comparison between PK-on-PK and PK-on-M bearing couples under physiologically relevant wear conditions, as may be expected *in-vivo* during standard gait following a TKR, is reported²².

All polymer bearings introduce different tribological challenges to those posed by the well documented 'hard-on-soft' bearings, for example, both bearing couples in this study are believed to be hydrophobic, influencing the wettability (the capacity of a fluid to maintain contact with a solid surface through the use of adhesive and cohesive forces, which can be determined *in-vitro* through measurement of the contact angle for the liquid-solid interface, enabling the wettability difference ($\Delta\theta$) for the bearing couples to be calculated). The wettability of lubricated polymers has an impact on both the wear and adhesion strength of polymer films, which affects the roughness of counter bearings and the amount of wear²³. As such, Borruto *et al.*²⁴ concluded that the wettability difference between materials proposed for use as a bearing couple for joint replacements is of importance and should also be taken into

consideration, therefore, this parameter was included as part of the analysis of the performance of the bearing combinations under test.

The aim of this study was to compare the wear rate and associated behaviours of PEEK-OPTIMA™ polymer from Invibio Limited articulating on PEEK-OPTIMA™ (PK-on-PK) and PEEK-OPTIMA™ on highly polished metal (PK-on-M) bearing combinations under physiologically relevant conditions of TKR. The specific research questions addressed were: What is the wear rate of PK-on-PK and PK-on-M bearings under uni-directional (zero CS) and multi-directional (CS) motion? What topographical changes are created from the introduction of CS for PK-on-PK and PK-on-M bearings? How does the surface wettability change as a result of topological changes due to wear between these different bearing combinations?

MATERIALS AND METHODS

For PK-on-PK wear tests PEEK-OPTIMA Natural polymer from Invibio Ltd, pins and counter face plates were used. The PEEK pins were machined from a 1 m long, 6.3 mm diameter rod to form 20 mm long, flat ended conical faced pins with an edge angle of 65° and contact diameter of 3 mm. Injection moulded PEEK plates were machined to 50 mm long, 25 mm wide and 5 mm deep cuboids. The machined PEEK pins had a mean, pre-test, 3 dimensional surface roughness (Sa) of < 2 µm and the plates a Sa < 0.04 µm. There was an increase in surface roughness for the pins due to the machining marks present from turning. The plates surfaces were not machined or finished in any way – they were ‘as moulded’. For the PK-on-M studies Stainless Steel 316 L metal plates, 50 mm long, 25 mm wide and 3 mm deep, were polished using a Buehler MetaServ 250 Grinder-Polisher to a mean Sa < 0.01 µm. All PEEK-OPTIMA™ test components (n = 4) were soaked in de-ionised water for a minimum of 35 days prior to test until steady state mass was achieved.

All tests were conducted on a four station multi-directional motion PoP test rig, Figure2, which

has previously been validated as capable of producing clinically relevant wear^{17,25,26}; the design and methodology of the PoP rig is detailed elsewhere^{17,27}. Test pins had a 20 mm sliding distance against test plates at a frequency of 1 Hz, and constant rotation of the pin perpendicular to the plate at either 0 or 1 Hz, where 1 Hz rotation resulted in multi-directional motion, (CS motion). New born calf serum (BCS) (Gibico™ Life Technologies, New Zealand) at 65 g/L protein concentration was diluted with de-ionised water to give 20 mL of BCS test lubricant per test cell equating to a 21 g/L protein concentration, to match that of human synovial fluid²⁸ and in conjunction with ISO 14243 – 1:2009 Implants for surgery – Wear of total knee-joint prostheses²⁹. A compressive load of 40 N was applied to lever arms which at the pin face resulted in a nominal contact pressure of 5.7 MPa. Tests were run to one million cycles (Mc) with the rig cleaned, lubricant (BCS) changed and wear assessed gravimetrically every 0.33 Mc. Unloaded soak control pins and plates (n = 3) were immersed in 33 % BCS and kept within the PoP rigs protective casing to ensure they were subject to the same temperature and moisture conditions as the test specimens, enabling accurate, soak-compensated wear data.

Prior to data collection, samples were cleaned using Virkon, iso-propanol, deionized water and an ultrasonic bath. Test pins were then left to air dry inside the PoP rigs protective casing for 48 hours, before being weighed. Wear was assessed gravimetrically using an analytical mass balance (TB-215D: Denver Instruments, Germany) with a sensitivity of 0.01 mg. Four repeats of each sample were recorded and the mean taken; this was then converted to volumetric wear (V) in mm³ by subtracting the mean increase in mass of the control pins and dividing by the density of PEEK (1.3 mg/mm³). The total sliding distance was then calculated using Equation 1 $D = (1/2) r \theta + \text{Linear Distance}$ which incorporates the rotation of the pins, giving a total sliding distance per cycle of 0.045 m, allowing the wear factor k (mm³/Nm) to be calculated using Equation 2, $k = V / (LD)$ where L is the load (N) and D is the total sliding distance for

147 the duration of the test (m).

148 The wettability of each material was determined through the measurement of the water contact
149 angle (WCA), θ , the interior angle formed tangential to the drop interface ²⁴ shown in Figure
150 1. The samples were cleaned with iso-propanol and left to air dry; static WCA measurements
151 were then taken, using distilled water on an Attension Optical Tensiometer TL-100 (Biolin
152 Scientific). Nine measurements were taken for each plate, and three for each of the pins,
153 including both the left and right WCAs from which the mean was taken. A 5 ± 1 μ L drop size,
154 air light phase, water heavy phase and ten second record time was used. Post-test
155 measurements were all taken from within the wear track.

156 Surface topography measurements were taken using a ZYGO NewView 5000 non- contacting
157 white light interferometer with a vertical resolution of more than 0.1 nm. The x10 objective
158 lens was used and combined with x2 manual zoom for metal and PEEK-OPTIMA plates and
159 x0.4 manual zoom for PEEK-OPTIMA pins. Nine readings of the Sa, the 3 dimensional area
160 measurement for the average surface roughness, were taken from the plates, using
161 approximately the same points as for the WCAs, and the mean taken for each bearing couple.
162 Five measurements were taken from the pins; one central point and one at each quadrant. To
163 examine the surface wear on both the PEEK-OPTIMA pins and plates, a scanning electron
164 microscope (SEM), Hitachi TM3030 with a spatial and depth resolution of < 100 nm and > 10
165 nm respectively, was used. This was combined with energy-dispersive X-ray spectroscopy
166 (EDX) to determine the elemental composition of any debris present. As no coatings were
167 used on the SEM a Brunel Microscope with digicam UCMOS and Touptek photonics AMA050
168 adjustable microscope adapter was used to illustrate the degree of pitting found on the PEEK-
169 OPTIMA plates. A x10 objective lens combined with a x10 optical was used.

Statistical Analysis was by analysis of variance (ANOVA) with a Tukey post hoc test with statistical significance taken when $p < 0.05$, using Minitab® 17.

RESULTS

The combined pin and plate wear factors are shown in Figure 3. Both the highest and lowest wear factor recorded was for the PK-on-M bearing couple, $(1.94 \pm 0.83) \times 10^{-6} \text{ mm}^3/\text{Nm}$ and $(15 \pm 7.60) \times 10^{-6} \text{ mm}^3/\text{Nm}$ (mean \pm standard deviation) under zero CS, and CS respectively. Under CS conditions there was a significant difference ($p < 0.02$) between the PK-on-PK and PK-on-M pin-only wear factors however, there was an insignificant difference ($p > 0.1$) when subject to zero CS. The combined wear of PK-on-PK and PK-on-M bearing combinations increased significantly ($p < 0.05$) when CS was introduced which was visibly noticeable on the wear tracks present on the PEEK plates when CS was introduced, Figure 4. Under both CS conditions, for PK-on-PK tests, PEEK-OPTIMA plates displayed the higher wear factor, showing a greater variability than the pins.

The wear factor for PEEK-OPTIMA pins articulating on polished metal plates was higher than that of the PEEK-OPTIMA pins articulating on PEEK-OPTIMA plates under both CS conditions, with a statistically significant increase ($p < 0.01$) for the PK-on-M pins when subject to CS, but not for the PK-on-PK pins, indicating that the counter face bearing material has a notable effect. A summary of the comparisons made between bearing couples and wear factors with statistical significance is shown in Table 1.

An example of the WCA measurements for PK-on-PK pins post-test is shown in Figure 5, all results in Figure 6 and the difference in wettability, $\Delta\theta$, between the two bearing couples shown in Table 2. The mean WCA for the PEEK-OPTIMA samples pre-test was $(86 \pm 4.6^\circ)$ (mean \pm standard deviation). The WCA for the metal plates pre-test was $(67 \pm 4.7^\circ)$ with a statistically

significant increase ($p < 0.05$) to $(73 \pm 1.9^\circ)$ under zero CS but reduced, with no statistical difference ($p > 0.05$), to $(64 \pm 2.1^\circ)$ when subject to CS. For the PK-on-PK tests there was a significant difference ($p < 0.05$) in the WCA for the plates, pre and post-test, whereas the pins showed minimal difference.

The surface roughness was also investigated; results shown in Figure 7. Following testing, for both test conditions, metal and PEEK-OPTIMA plates increased in Sa; ($p > 0.05$) and ($p < 0.05$) respectively, whilst all PEEK-OPTIMA pins decreased in Sa ($p < 0.05$). The latter is due to an elimination of machining marks which were replaced with parallel wear lines in the direction of motion when no CS was applied as shown in Figure 8. This is in comparison to the CS tests, where a smoother polished appearance was observed on the PEEK-OPTIMA pins. Post-test Sa for both the metal plates and PK pins from the PK-on-M bearing couples subject to CS and no CS only differed by $< 0.1 \mu\text{m}$.

Scanning electron microscopy images from the PK-on-PK wear tests showed evidence of pitting and the early formation of wear debris; where debris was present on the wear surfaces, as indicated in Figure 9, EDX analysis was performed. Carbon and oxygen confirmed the presence of PEEK particles, whereas nitrogen was unexpected. The degree of pitting is shown in Figure 10.

DISCUSSION

Although M-on-P bearings are currently the gold standard for knee replacements, polyethylene wear resulting in osteolysis and aseptic loosening remains an important issue. In order to assess PEEK as a potential bearing this study has compared the effects of uni-directional motion (zero CS) and multi-directional motion (CS) on PK-on-PK and PK-on-M bearing couples under

identical, physiologically relevant test conditions with a contact pressure of 5.7 MPa, similar to that during normal gait following a TKR²². However, it should be noted that peak contact stresses, > 25 MPa, found during stair climb or squatting (deep flexion) are also possible *in-vivo*³⁰.

Under zero CS, wear factors for the PEEK-OPTIMA pins of the PK-on-PK and PK-on-M studies were $(1.62 \pm 1.28) \times 10^{-6} \text{ mm}^3/\text{Nm}$ and $(1.94 \pm 0.83) \times 10^{-6} \text{ mm}^3/\text{Nm}$ respectively (Figure 3). After CS was introduced a non-significant ($p > 0.05$) increase in the wear of the PK-on-PK test pins to $(3.91 \pm 1.28) \times 10^{-6} \text{ mm}^3/\text{Nm}$ was recorded. Conversely, a significant ($p < 0.05$) increase in the wear factor of the PK-on-M pins was observed $(15.01 \pm 7.60) \times 10^{-6} \text{ mm}^3/\text{Nm}$. The increase in wear factor for the PK-on-PK and PK-on-M pins when subject to CS was 241.40 % and 773.71 % respectively. This difference suggests that a hard counter face bearing material directly effects the CS dependency and wear factor of PEEK-OPTIMA bearings. This confirms the effect reported by Brockett *et al.*²¹. There was no significant CS dependency observed for PEEK-OPTIMA pins when articulating on the PEEK-OPTIMA counter face lubricated with a proteinaceous fluid (BCS) in this study, which is a similar characteristic to the results reported by Baykal *et al.*²⁰ for the all-polymer, PEEK-OPTIMA and polyethylene bearing combinations, and those reported by Laux and Schwartz³¹ under dry lubricated conditions, however, at a lower contact pressure of 1.1 MPa. The lack of a significant change in the behaviour of these all-polymer combinations whether wet or dry, may suggest that the lubrication regime and wear mechanism is not influenced greatly by protein content of the test lubricant, but more so by the contact pressure applied under dry/lubricant starved conditions as Laux and Schwartz³¹ reported a significant cross shear dependency when tested at 5.1 MPa. Further investigations into both the contact pressure and lubricant protein content are required.

239 The PK-on-M wear results presented here are in agreement with those in the literature from
240 Brockett *et al.*²¹ who found a wear factor of $(1.76 \pm 2.29) \times 10^{-6} \text{ mm}^3/\text{Nm}$ for PK-on-M under
241 zero CS conditions, with an increase to $(7.29 \pm 2.18) \times 10^{-6} \text{ mm}^3/\text{Nm}$ when CS was applied.
242 However, this was with a lower contact pressure of 4 MPa.

243 The wear factor of the PEEK-OPTIMA bearing surfaces were much more influenced by CS
244 when articulating on the harder metal counter-faces than when articulating against the softer
245 PEEK-OPTIMA counter-faces. This may be because the harder polished metal counter-face
246 can frictionally drag the polymer chains into a 'strain hardened' linear arrangement, increasing
247 the resistance to wear, as demonstrated by Wang *et al.*¹⁹ for UHMWPE when subject to
248 adhesive wear. However, a more sophisticated analysis is necessary to determine this under
249 carefully controlled conditions in a following study. This is in contrast to the PK-on-PK
250 bearing couples which were much less CS dependent than the PK-on-M, as the two interacting
251 bearing surfaces hold their polymer chain with a similar force, limiting the effect of strain
252 hardening on one of the bearing couples. Moreover, there was approximately an order of
253 magnitude increase in the wear factor for the PK-on-M bearing couple when subject to CS,
254 compared to similar tests on UHMWPE which typically yield an increase of two orders of
255 magnitude due to the strain hardening effect¹⁸. It is therefore concluded that PEEK is
256 displaying a CS dependant behaviour in a similar manner to UHMWPE but to a lesser extent
257 and the mechanical process may or may not be similar. This effect raises important
258 considerations for future orthopaedic bearing designs that utilise PEEK materials.

259 Despite the lower Sa of the metal plates the total PK-on-M wear factor $(15.01 \pm 7.60) \times 10^{-6}$
260 mm^3/Nm was higher than the PK-on-PK total wear factor $(7.93 \pm 2.62) \times 10^{-6} \text{ mm}^3/\text{Nm}$ under
261 CS conditions. It is possible that frictional heating was produced by the high friction all

polymer bearing couple³² potentially causing protein precipitation leading to a protective layer of precipitated proteins reducing the wear^{20,33}. However, this could be due to an artefact of testing, which only occurred due to the continuous cyclic loading, 250, 000 cycles, which would not happen *in-vivo*³³.

A study by Brockett *et al*³⁴ reported mechanical failure of PEEK when articulating against a metallic counterface, concluding that PK-on-M does not offer improvement as an alternative bearing couple compared to the conventional UHMWPE-on-M. This is also true for this study where the wear factors of PK-on-M were higher than those reported for the conventional UHMWPE-on-M conducted under similar test conditions on PoP test rigs ($1.8 \times 10^{-7} - 1.1 \times 10^{-6}$) mm³/Nm^{17,19,35,36}.

Evidence of wear was apparent on both PEEK-OPTIMA plates and pins. Signs of scratching was visible within the wear tracks of the PEEK-OPTIMA plates and parallel lines in the direction of sliding were observed on the zero CS test pins, whilst pins subject to CS had a smoother glossy appearance. There was a notable difference in the wear tracks of the PEEK-OPTIMA plates when subject to CS; plates from zero CS tests had very slight wear tracks compared to the well-defined wear tracks for the multi-directional motion (Figure 4). Furthermore, the zero CS plates had a dull appearance compared to the burnished wear tracks observed on the plates subject to CS. This could be due to work-hardened wear particles acting as third body wear debris³⁷.

Scanning electron microscopy images of both pins and plates, post-test, confirmed evidence of debris on the surface. EDX analysis during SEM investigation found Carbon and Oxygen present on the surface suggesting the debris was PEEK-OPTIMA wear particles as shown in

Figure 9, however, as Nitrogen was also found, and is not part of the PEEK molecule, further work is required to investigate its presence. Possible sources could be contamination from air or from the proteins in the BCS. There was also evidence of material build up at the edge of the wear tracks on the PEEK-OPTIMA plates during zero CS PK-on-PK tests, displaying evidence of creep deformation, as seen at x1800 magnification (Figure 9).

The surface roughness and WCA were also investigated, as increasing the surface roughness of a material can have a significant effect on the WCA. The mean WCA \pm standard deviation for the PEEK-OPTIMA samples prior to test was $(86 \pm 4.6^\circ)$ which is similar to that found by Novotna *et al.*³⁸ who found the wettability of PEEK-OPTIMA pre-test to be approximately 79.5° and in contrast to Borruto *et al.*,²⁴ who reported a WCA of 65° , suggesting a more hydrophilic surface ($\theta < 90^\circ$). Theoretically, as stated by Wenzel's model, when considering a hydrophilic material, such as the metal plates in this study, due to the chemistry of the surface, an increase in surface roughness and decrease in WCA should lead to an enhanced wettability, as when $\theta < 90^\circ$ liquid can penetrate the pores of the solid, filling them up forming a plane surface, part solid part liquid³⁹. This is in contrast to a hydrophobic surface where, ($90^\circ < \theta < 180^\circ$), for the WCA, and the Cassie Baxter theory applies as gas molecules can become entrapped in some of the asperities of the surface preventing the liquid from penetrating all the pores. However, for the true Cassie Baxter model to apply there should be no penetration of the liquid into the grooves^{40,41}. This leads to a mixture of solid-liquid and solid-gas interfaces, and an increase in surface roughness leading to an increase in WCA, increasing the hydrophobicity of the material surface⁴².

Due to the difference in wettability, ($\Delta\theta$) between the two surfaces, the PK-on-M bearing couple should have the most efficient lubrication due to the stable film produced between the

hydrophobic and hydrophilic surfaces. This was confirmed experimentally by Borruto *et al.*²⁴ and observed under zero CS testing in this study. The biggest difference in wettability in this study was for the PK-on-M when subject to CS ($\Delta\theta = 19^\circ$), suggesting that when subject to CS the PK-on-M should have benefitted from this change; however, the PK-on-M bearing couple subject to CS produced the highest wear factor recorded for this study, $(1.5 \pm 0.76) \times 10^{-5} \text{ mm}^3/\text{Nm}$. Even so, it is feasible that the wear may have been even higher if the advantageous wettability was not present. A weak trend noted for the wettability difference is that as PEEK-OPTIMA wears it gradually becomes more hydrophilic (Figure 6).

For the PK-on-M tests, the hydrophobic PEEK-OPTIM pins displayed a decrease in surface roughness with corresponding decrease in WCA as expected; however, the hydrophilic plates saw an increase in surface roughness and increase in WCA, which was unexpected, as an increase in surface roughness should lead to a decrease in WCA for hydrophilic materials⁴³. It is postulated that this could be due to a PEEK-OPTIMA polymeric film transferring onto the surface of the metal plate. This would also support the supposition that adhesive wear has taken place.

CONCLUSION

In conclusion, this study suggests that the wear rate of PEEK-OPTIMA, under physiologically relevant parameters similar to TKR *in-vivo*, is CS dependent when articulating on hard polished counter bearings and less CS dependent when articulating on softer PEEK-OPTIMA counter bearings. As such, when subject to CS environments, as seen in fixed bearing TKR, PK-on-M does not offer the most favourable alternative to the conventional UHMWPE-on-M. However, under lower CS conditions, as seen in rotating platform knees, PK-on-PK may offer a metal free alternative bearing couple with a reduction in stress shielding. The concept of an all-polymer bearing couple warrants further investigation as there are considerations, other than

331 tribology alone, which would be advantageous to an all-polymer bearing, such as cost,
332 biocompatibility, radiolucency and elimination of risks for patients suffering from metal
333 hypersensitivity.

334 **ACKNOWLEDGEMENTS**

335 The authors acknowledge the help given by Mike Foster for the SEM images, Victoria
336 Chamberlain for the microscope images, James Rose and Brian Stoker for the machining work
337 and Lewis Woollin for the PoP Schematic diagram (Figure 2).

338 **FUNDING AND DECLARATION OF INTEREST**

339 This work was funded by The School of Engineering (Mechanical), Newcastle University as
340 part of a PhD project with Invibio Ltd who provided the PEEK OPTIMA samples. Dr Adam
341 Briscoe is a paid employee of Invibio Limited. INVIBIO™, PEEK-OPTIMA™, and INVIBIO
342 BIOMATERIAL SOLUTIONS™ are trademarks of Victrex plc or its group companies. All
343 rights reserved.

REFERENCES

1. National Joint Registry for England, Wales and Northern Ireland. National Joint Registry 14th annual report, 2017, <http://www.njrreports.org.uk/Portals/0/PDFdownloads/NJR%2014th%20Annual%20Report%202017.pdf> (accessed 12 April 2018).
2. Hyde PJ, Fisher J, Hall RM. Wear characteristics of an unconstrained lumbar total disc replacement under a range of in vitro test conditions. *J Biomed Mater Res B Appl Biomater* 2017;105(1):46-52.
3. Green TR, Fisher J, Matthews JB, Stone MH, Ingham E. Effect of size and dose on bone resorption activity of macrophages by in vitro clinically relevant ultra high molecular weight polyethylene particles. *J Biomed Mater Res* 2000;53(5):490-7.
4. Toth JM, Wang M, Estes BT, Scifert JL, Seim HB, 3rd, Turner AS. Polyetheretherketone as a biomaterial for spinal applications. *Biomaterials* 2006;27(3):324-34.
5. Ponnappan RK, Serhan H, Zarda B, Patel R, Albert T, Vaccaro AR. Biomechanical evaluation and comparison of polyetheretherketone rod system to traditional titanium rod fixation. *Spine J* 2009;9(3):263-7.
6. Kraft M. Impact of the Processing History on the Wear Performance of a PEEK-on-PEEK Bearing for Cervical Total Disc Replacement. *J. Mechanics* 2013;3(5A):1-7
7. Kraft M, Koch DK, Bushelow M. An investigation into PEEK-on-PEEK as a bearing surface candidate for cervical total disc replacement. *Spine J* 2012;12(7):603-611.
8. Grupp TM, Meisel H-J, Cotton JA, Schwiesau J, Fritz B, Blömer W, Jansson V. Alternative bearing materials for intervertebral disc arthroplasty. *Biomaterials* 2010;31(3):523-531.
9. Brown T, Bao Q-B. The use of self-mating PEEK as an alternative bearing material for cervical disc arthroplasty: a comparison of different simulator inputs and tribological environments. *Eur Spine J* 2012;21(Suppl 5):717-726.
10. Kurtz SM, *Plastics Design Library. PEEK biomaterials handbook*. Oxford UK ; Waltham, MA: William Andrew; 2012. x, 298 p. p.
11. Kurtz SM, Devine JN. PEEK Biomaterials in Trauma, Orthopedic, and Spinal Implants. *Biomaterials* 2007;28(32):4845-4869.
12. Ogawa M, Tohma Y, Ohgushi H, Takakura Y, Tanaka Y. Early fixation of cobalt-chromium based alloy surgical implants to bone using a tissue-engineering approach. *Int J Mol Sci* 2012;13(5):5528-41.
13. Cowie RM, Briscoe A, Fisher J, Jennings LM. PEEK-OPTIMA as an alternative to cobalt chrome in the femoral component of total knee replacement: A preliminary study. *Proc Inst Mech Eng H* 2016;230(11):1008-1015.

14. Moore DJ, Freeman MAR, Revell PA, Bradley GW, Tuke M. Can a total knee replacement prosthesis be made entirely of polymers? *The J Arthroplasty* 1998;13(4):388-395.
15. de Ruiter L, Janssen D, Briscoe A, Verdonshot N. A preclinical numerical assessment of a polyetheretherketone femoral component in total knee arthroplasty during gait. *J Exp Orthop* 2017;4(1):3.
16. Wang A, Sun DC, Yau SS, Edwards B, Sokol M, Essner A, Polineni VK, Stark C, Dumbleton JH. Orientation softening in the deformation and wear of ultra-high molecular weight polyethylene. *Wear* 1997;203–204:230-241.
17. Joyce TJ, Monk D, Scholes SC, Unsworth A. A multi-directional wear screening device and preliminary results of UHMWPE articulating against stainless steel. *Biomed Mater Eng* 2000;10(3-4):241-9.
18. Kang L, Galvin AL, Brown TD, Jin Z, Fisher J. Quantification of the effect of cross-shear on the wear of conventional and highly cross-linked UHMWPE. *J Biomech* 2008;41(2):340-6.
19. Wang A. A unified theory of wear for ultra-high molecular weight polyethylene in multi-directional sliding. *Wear* 2001;248(1-2):38-47.
20. Baykal D, Siskey RS, Underwood RJ, Briscoe A, Kurtz SM. The Biotribology of PEEK-on-HXLPE Bearings Is Comparable to Traditional Bearings on a Multidirectional Pin-on-disk Tester. *Clin Orthop Relat Res* 2016;474(11):2384-2393.
21. Brockett CL, Carbone S, Abdelgaied A, Fisher J, Jennings LM. Influence of contact pressure, cross-shear and counterface material on the wear of PEEK and CFR-PEEK for orthopaedic applications. *J Mech Behav Biomed Mater* 2016;63:10-6.
22. Abdelgaied A, Fisher J, Jennings LM. A comprehensive combined experimental and computational framework for pre-clinical wear simulation of total knee replacements. *J Mech Behav of Biomed Mater* 2018;78:282-291.
23. Cooper JR, Dowson D, Fisher J. The effect of transfer film and surface roughness on the wear of lubricated ultra-high molecular weight polyethylene. *Clin Mater* 1993;14(4):295-302.
24. Borruto A, Marrelli L, Palma F. The difference of material wettability as critical factor in the choice of a tribological prosthetic coupling without debris release. *Tribology Letters* 2005;20(1):1-10.
25. Scholes SC, Unsworth A. Wear studies on the likely performance of CFR-PEEK/CoCrMo for use as artificial joint bearing materials. *J Mater Sci Mater Med* 2009;20(1):163-70.
26. Scholes SC, Unsworth A. Pin-on-plate studies on the effect of rotation on the wear of metal-on-metal samples. *J Mater Sci Mater Med* 2001;12(4):299-303.

27. Scholes SC, Unsworth A. The wear properties of CFR-PEEK-OPTIMA articulating against ceramic assessed on a multidirectional pin-on-plate machine. *Proc Inst Mech Eng H* 2007;221(3):281-9.
28. Decker B, Mc KB, Mc GW, Slocumb CH. Comparative distribution of proteins and glycoproteins of serum and synovial fluid. *Arthritis Rheum* 1959;2(2):162-77.
29. ISO 14243-1:2009 Implants for surgery -- Wear of total knee-joint prostheses -- Part 1: Loading and displacement parameters for wear-testing machines with load control and corresponding environmental conditions for test. International Standards Organisation: Geneva, Switzerland, 2009.
30. Thambyah A, Goh JCH, De SD. Contact stresses in the knee joint in deep flexion. *Med Eng Phys* 2005;27(4):329-335.
31. Laux KA, Schwartz CJ. Influence of linear reciprocating and multi-directional sliding on PEEK wear performance and transfer film formation. *Wear* 2013;301(1-2):727-734.
32. Hyde PJ, Fisher, J., Hall, R.M. Friction of PEEK and Carbon Fibre Reinforced PEEK Bearing Couples under Contact Conditions Typical of the Cervical Spine. 7th World Congress of Biomechanics. Boston, MA, USA 2014. Retrieved from https://eprint.ncl.ac.uk/pub_details2.aspx?pub_id=216562
33. Lu Z, McKellop H. Frictional heating of bearing materials tested in a hip joint wear simulator. *Proc Inst Mech Eng H* 1997;211(1):101-108.
34. Brockett CL, Carbone S, Fisher J, Jennings LM. PEEK and CFR-PEEK as alternative bearing materials to UHMWPE in a fixed bearing total knee replacement: An experimental wear study. *Wear* 2017;374-375:86-91.
35. Abdelgaied A, Brockett CL, Liu F, Jennings LM, Fisher J, Jin Z. Quantification of the effect of cross-shear and applied nominal contact pressure on the wear of moderately cross-linked polyethylene. *Proc Inst Mech Eng H* 2013;227(1):18-26.
36. Vassiliou K, Unsworth A. Is the wear factor in total joint replacements dependent on the nominal contact stress in ultra-high molecular weight polyethylene contacts? *Proc Inst Mech Eng H* 2004;218(2):101-7.
37. Hyde PJ, Tipper J, Fisher J, Hall RM. Wear and biological effects of a semi-constrained total disc replacement subject to modified ISO standard test conditions. *J Mech Behav Biomed Mater* 2015;44:43-52.
38. Novotna Z, Reznickova A, Rimpelova S, Vesely M, Kolska Z, Svorcik V. Tailoring of PEEK bioactivity for improved cell interaction: plasma treatment in action. *RSC Advances* 2015;5(52):41428-41436.
39. Shaw DJ. 6 - The solid-liquid interface. *Introduction to Colloid and Surface Chemistry (Fourth Edition)*. Oxford: Butterworth-Heinemann; 1992. p 151-173.

40. Tuteja A, Choi W, Ma M, Mabry JM, Mazzella SA, Rutledge GC, McKinley GH, Cohen RE. Designing Superoleophobic Surfaces. *Science* 2007;318(5856):1618.
41. Baxter CABDaS. Wettability of porous surfaces. *Transactions of the Faraday Society*; 1944.
42. Kubiak KJ, Wilson MCT, Mathia TG, Carval P. Wettability versus roughness of engineering surfaces. *Wear* 2011;271(3-4):523-528.
43. Wenzel RN. RESISTANCE OF SOLID SURFACES TO WETTING BY WATER. *Industrial & Engineering Chemistry* 1936;28(8):988-994.

FIGURE CAPTIONS

Figure 1: Contact angle measurements using Young's equation for a smooth surface

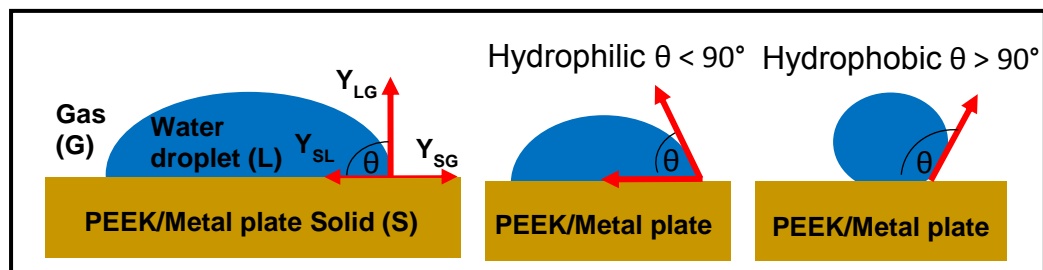


Figure 2: Schematic of the four station multi-directional pin-on-plate test rig. (A) AC motor, (B) crankshaft, (C) plate holder (D) test plate, (E) pin holders, (F) DC motor, (G) lever arm, (H) worm reduction gear

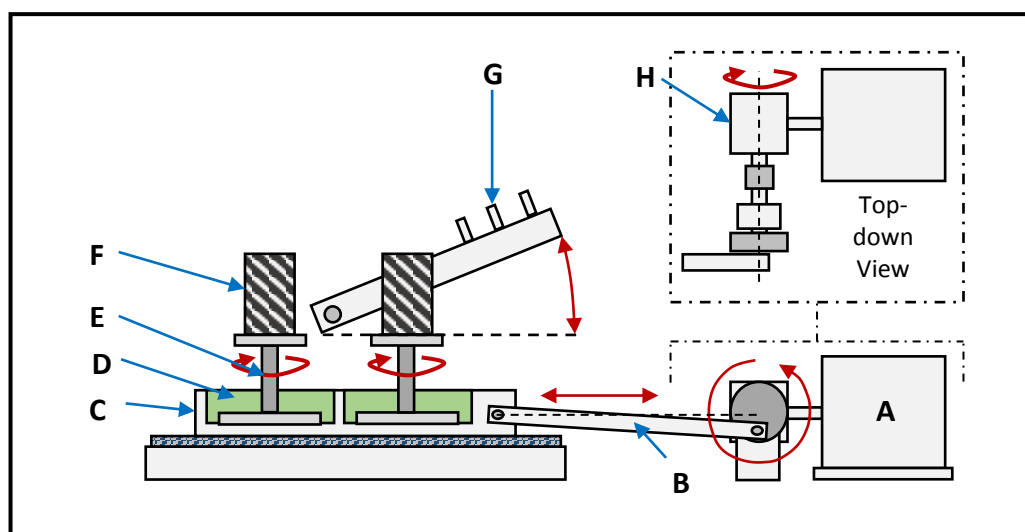


Figure 3: Mean (n=4) wear factors for PK-on-PK and PK-on-M bearing couples under CS and zero CS. Error bars represent \pm standard deviation

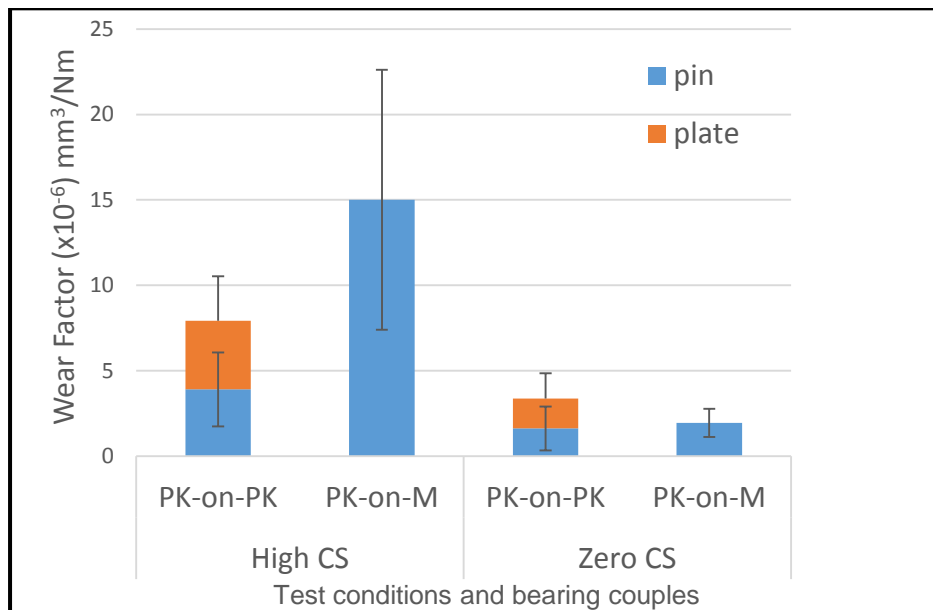


Figure 4: Wear tracks from the PK-on-PK wear test. Left soak control, (middle) Zero CS and (right) CS

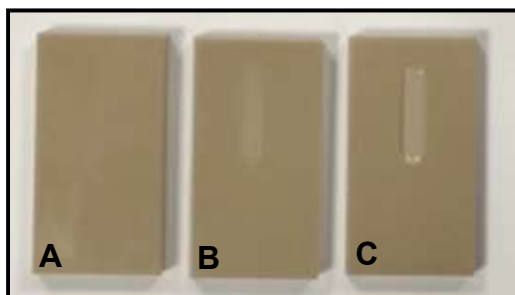


Figure 5: Water contact angle for PK-on-PK pins post-test (A) zero CS and (B) CS

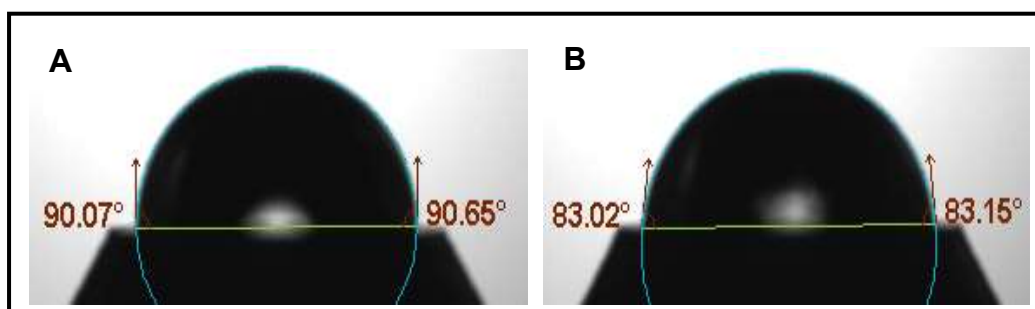


Figure 6: Mean (n=4) water contact angle, WCA, values pre and post-test. Error bars represent \pm standard deviation

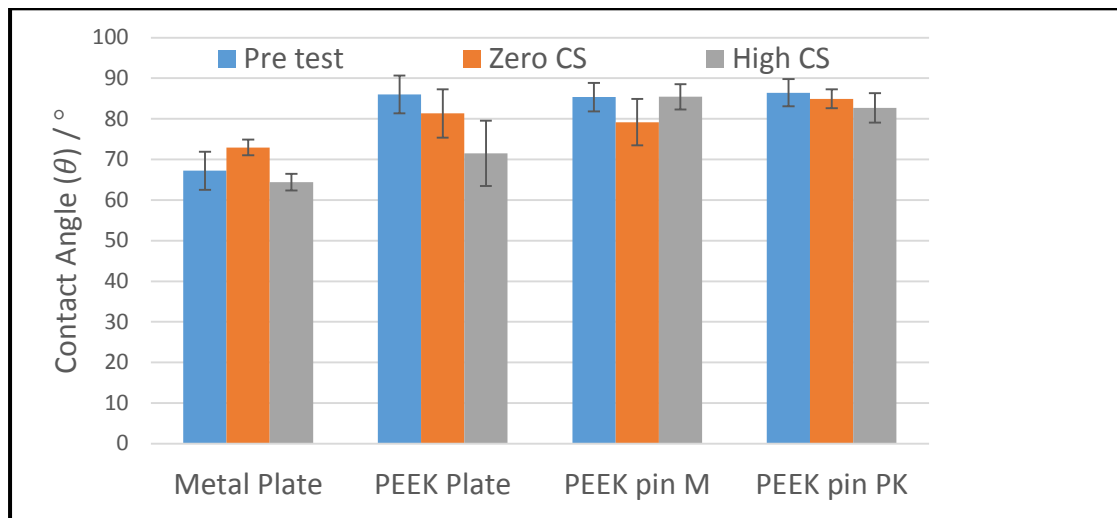


Figure 7: Mean (n=4) surface roughness, Sa, values pre and post-test. Error bars represent \pm standard deviation

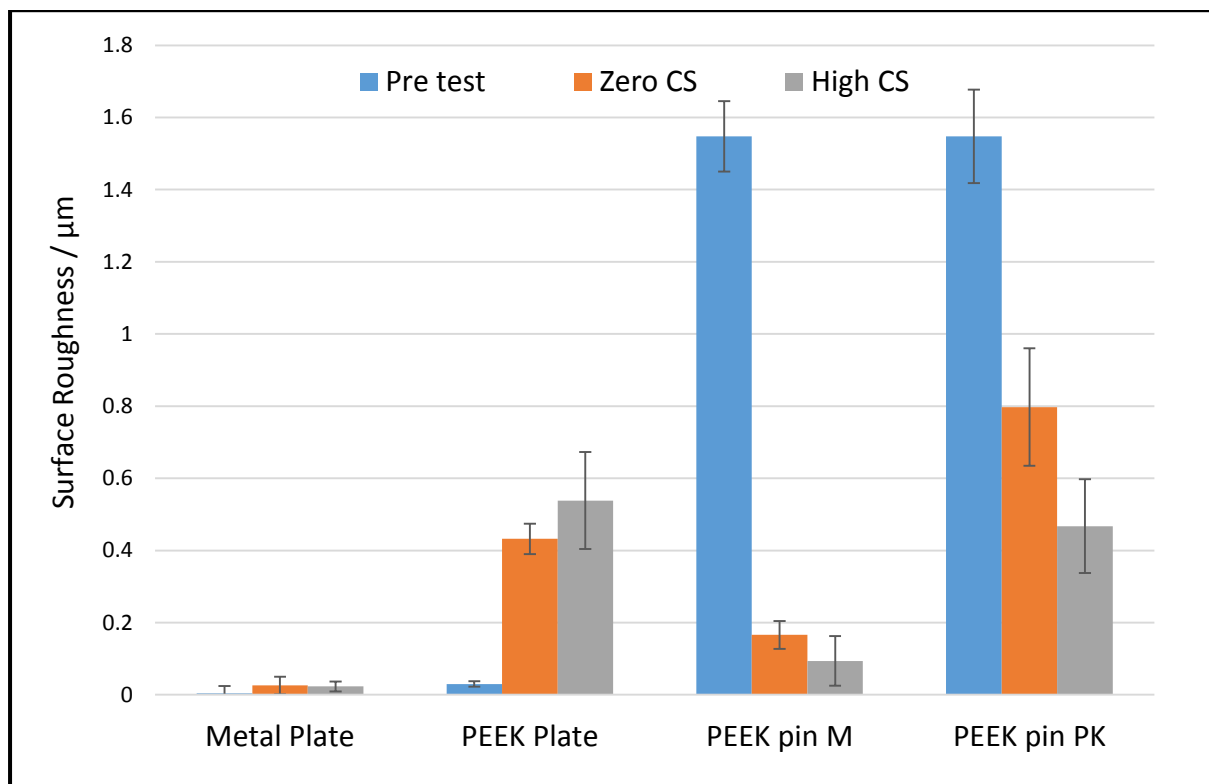


Figure 8: A Zygo oblique plot (A) and image (B) of PK-on-PK pins pre-test with machining marks present and post-test oblique plot (C) and image (D) displaying marks parallel to the direction of sliding

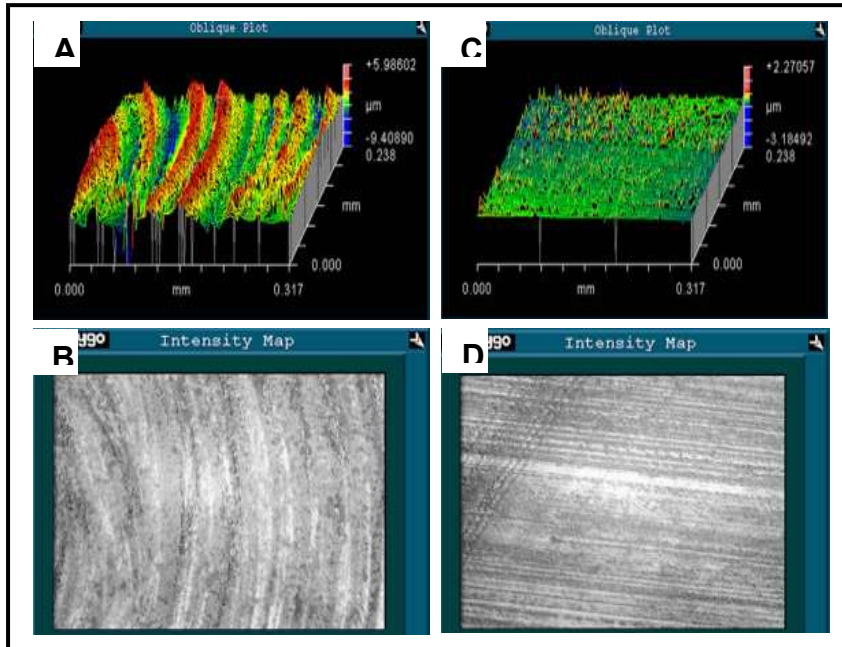


Figure 9: SEM images of a PK-on-PK pin post-test zero CS (A) with EDX analysis (B). A wear track of the PK-on-PK zero CS plate at x 80 magnification (C) and x 1800 magnification (D). Images were taken at 45°

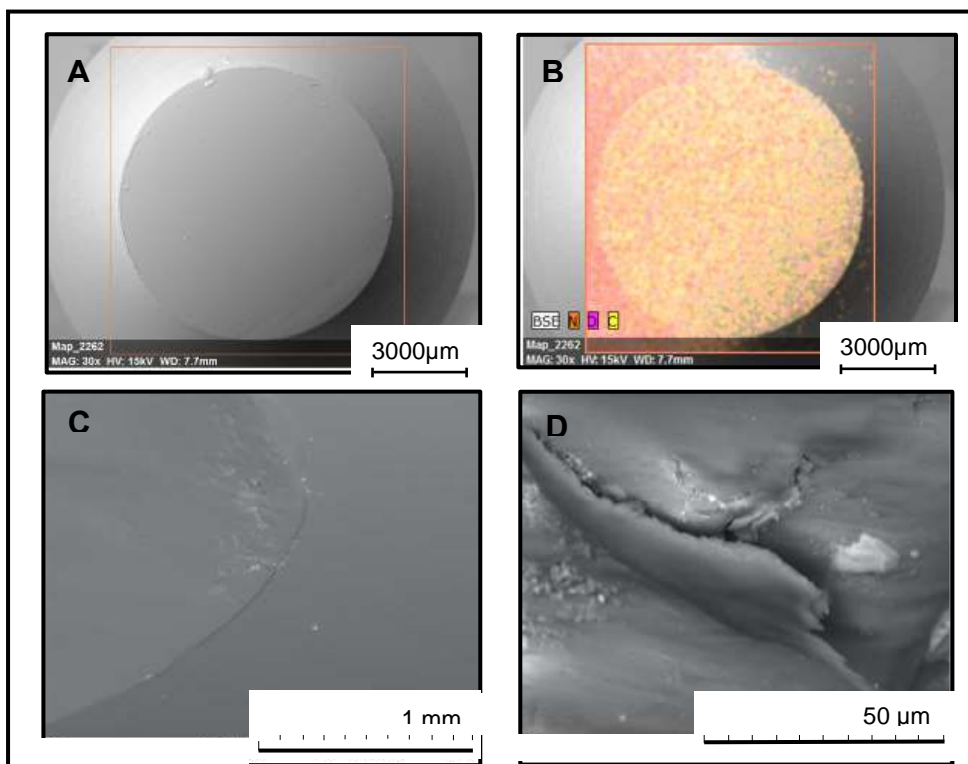


Figure 10: Microscopic images of pitting present on a PK-on-PK zero CS plate at 100 x magnification

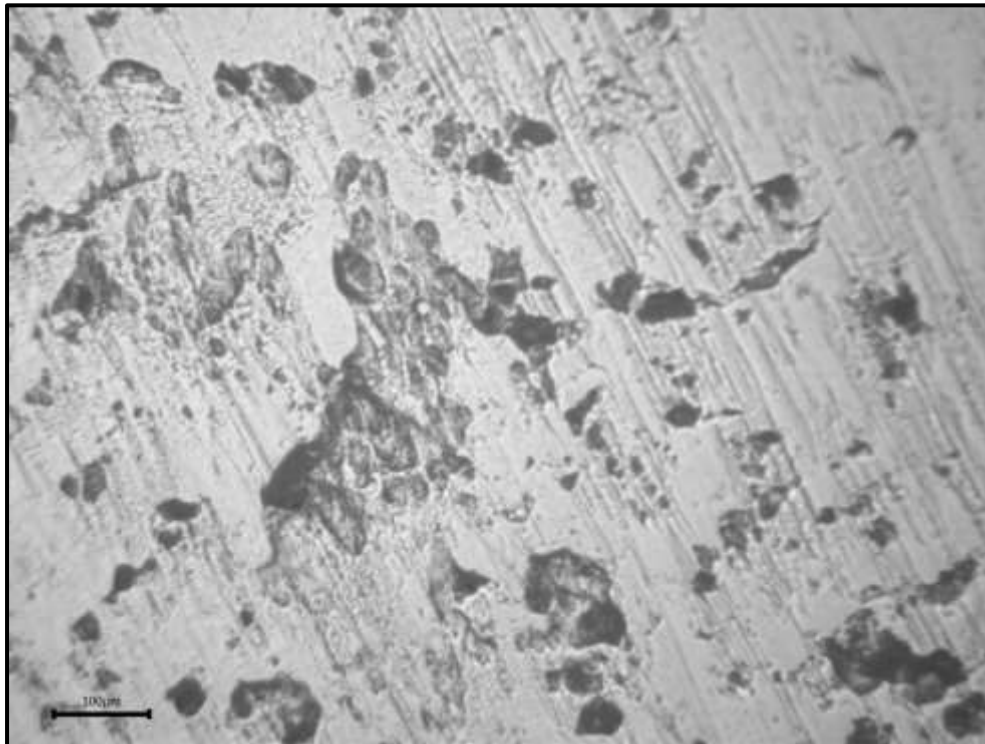


Table 1: Statistical significance between the different bearing couples and CS conditions tested

Bearing	Component	Test	Significant
PK-on-PK vs PK-on-M	Pin	CS	Yes
PK-on-PK vs PK-on-M	Pin	Zero CS	No
PK-on-PK	Pin	Zero CS vs CS	No
PK-on-M	Pin	Zero CS vs CS	Yes
PK-on-PK	Pin and plate	Zero CS vs CS	Yes
PK-on-M	Pin and plate	Zero CS vs CS	Yes

Table 2: Wettability for PK-on-PK and PK-on-M bearing couple's pre and post test

Bearing Couple	Wettability ($\Delta \theta$)		
	Pre Test	Zero CS	High CS
PK-on-M	18	10	19
PK-on-PK	0	6	9

Equation 1: Calculation of the total sliding distance per cycle of the pins

Equation 2: Calculation of the wear factor $k \text{ mm}^3/\text{Nm}$